

Degradation of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ Cathode Surfaces at Elevated Temperatures

Robert Kostecki and Frank McLarnon
Lawrence Berkeley National Laboratory
Berkeley, CA 94720, USA

The U.S. Department of Energy's Advanced Technology Development (ATD) Program is evaluating high-power lithium-ion batteries designed for use in hybrid-electric vehicles. Numerous 18650-size ATD cells containing carbon anodes, $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathodes, and DEC-EC-LiPF₆ electrolyte were tested under a variety of conditions and then characterized to identify failure mechanisms [1]. We used atomic force microscopy (AFM), current-sensing atomic force microscopy (CSAFM), and Raman microscopy to characterize changes of the $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathode surface.

Topographic AFM images of cathodes taken from cells which were cycle-life tested at $\geq 40^\circ\text{C}$ revealed significant changes in surface morphology (left-hand side of Fig. 1). The initial large and flat grains of cathode material are still recognizable, but the entire cathode surface became covered by nanocrystalline (50-200 nm) deposits. These deposits not only accumulated in the inter-granular spaces, but also were scattered randomly across the oxide grains. The amount of deposit and the extent of morphology change increased at higher cell test temperatures.

These cathode surface morphology changes were accompanied by a significant decrease of cathode surface electronic conductance. We employed CSAFM, which uses a conducting AFM tip to detect local electronic conductance, to produce a conductance map of the same electrode surface region (right-hand side of Fig. 1). The AFM images show a modest morphology change after the electrode was cycled, compared to the CSAFM maps which reveal a major decrease of surface conductance, signaled by a preponderance of light-colored (low-conductivity) regions. The electrode surface conductance was found to decrease as the batteries lost power during accelerated cycle-life tests. CSAFM measurements showed that the average conductance decreased significantly with increased cell test temperature, contributing to the impedance rise of the cathode. These observations provide strong evidence that processes at the electrode surface may play an important role in battery power loss, and will help direct future investigations into the detailed process mechanism(s) responsible for the loss.

An analysis of Raman microscope spectra of tested cathodes was carried out. Reference micro-Raman spectra of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ powders typically exhibit a broad maximum centered at $\sim 520\text{ cm}^{-1}$ with a sharp peak at $\sim 555\text{ cm}^{-1}$. Such spectral characteristics are typical for a solid solution of cobalt-substituted nickel oxides, rather than a mixture of new crystalline phases. We observed small variations of the shape of the broad peak at 520 cm^{-1} among different powder samples, and to a lesser extent between different grains in a given $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ powder sample. These inhomogeneities probably arise from slight variations of surface composition and structure of the $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ grains. For comparison, the Raman spectra of LiNiO_2 and LiCoO_2 powders exhibit pairs of well-defined vibration peaks at 468, 546 and 487, 597 cm^{-1} ,

respectively.

Micro-Raman spectra of the $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathodes extracted from Li-ion cells which were stored or cycled at $\geq 40^\circ\text{C}$ display significant changes. The originally featureless broad maximum at 520 cm^{-1} was split into separate peaks at 479, 553, and 565 cm^{-1} , and a weak shoulder at $\sim 600\text{ cm}^{-1}$. We determined that a thermally induced surface phase segregation process is responsible for this spectral behavior.

Substitution of Co for Ni does not change the R3m space group symmetry of the composite $\text{LiNi}_y\text{Co}_{1-y}\text{O}_2$ oxide, neither does the lithium intercalation-deintercalation process. However, from our studies of $\text{Li}_x\text{Ni}_{1-y}\text{Co}_y\text{O}_2$ systems we determined that Co substitution for Ni(III) oxides increases the crystal lattice parameter, as reflected by a 3-4 cm^{-1} shift of two $474/554\text{ cm}^{-1}$ peaks (characteristic of NiO_2) toward lower frequencies and an increased $474/554$ peak ratio. We found that lithium intercalation into the NiO_2 crystal lattice has quite the opposite effect, *i.e.*, the peaks shift slightly toward higher frequencies and the $474/554$ peak ratio decreases. The presence of separate peaks on both sides of the original NiO_2 peaks and strong variations in relative peak intensity in the spectra of these cathodes suggest the formation of stable crystalline phases of Ni(III) or Ni(IV) oxides with different amounts of cobalt and lithium on the $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathode surface.

Acknowledgement

This work was supported by the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

Reference

1. X. Zhang, P.N. Ross Jr., R. Kostecki, F. Kong, S. Sloop, J.B. Kerr, K. Striebel, E. J. Cairns, and F. McLarnon, *J. Electrochem. Soc.*, accepted for publication.

Figure 1. CSAFM images of a $5 \times 5\text{ }\mu\text{m}$ region of a $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathode, showing topography and surface conductance: (A) a fresh cell, (B) a cell cycled at 70°C . The dark areas on the conductance images indicate a conductive surface, whereas the lighter color indicates a major loss of surface conductance

